THE DISSOCIATION OF METHOXY-SUBSTITUTED HEXAARYLETHANES

BY

JOHN WALTER WHITSON, JR.

B.S., Beloit College, 1939
M.S., University of Illinois, 1941

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

URBANA, ILLINOIS
1943

THE DISSOCIATION OF METHOXY-SUBSTITUTED HEXAARYLETHANES

BY

JOHN WALTER WHITSON, JR.
B.S., Beloit College, 1939
M.S., University of Illinois, 1941

AN ABSTRACT OF A THESIS
SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1943

URBANA, ILLINOIS
1943

ACKNOWLEDGMENT

The writer expresses his sincere appreciation to Professor C. S. Marvel for his encouragement and guidance throughout the course of this investigation.

THE DISSOCIATION OF METHOXY-SUBSTITUTED HEXAARYLETHANES

Introduction

Since the time of Gomberg's[1] discovery of triphenylmethyl there have been several theories proposed to explain why hexaarylethanes undergo a reversible dissociation into free radicals Postulations have been made concerning the effects of resonance, electronic structure and the electronegativity of groups substituted in the phenyl nuclei.

In order to obtain additional information on the factors which effect the dissociation of hexaarylethanes, placing particular emphasis on the question of electronegativity, this study of the methoxy-substituted hexaarylethanes was undertaken. Although the investigation was primarily concerned with the aforementioned compounds, nevertheless, preliminary work was done on compounds representing other phases of the free radical problem in general.

Experimental and Discussion of Results

All of the triarylcarbinols were prepared through the use of Grignard reagents, and the corresponding chloromethanes were derived from the carbinols through treatment of the latter with acetyl chloride. Using the chloromethanes as starting materials several hexaphenylethanes containing methoxy substituents have been prepared in solution and the degrees of dissociation have been measured at a temperature of 25°C.[2] The solutions used in the magnetic susceptibility measurements were 0.1 *M*. The following ethanes and their dissociations are recorded: di-*o*-methoxyphenyltetraphenylethane (4 ± 1%), di-*m*-methoxyphenyltetraphenylethane (3 ± 1%), di-*p*-methoxyphenyltetraphenylethane (4 ± 1%), diphenyltetra-*o*-methoxyphenylethane (7 ± 1%), hexa-*o*-methoxyphenylethane (40 ± 5%), hexa-*m*-methoxyphenylethane (7 ± 1%).

Although all of these ethanes show a greater degree of dissociation than hexaphenylethane itself, the efficacy of the

methoxy group in promoting the dissociation is evidently not great. The effect of an *ortho* methoxy group is not much different from that of a *para* methoxy group, consequently it must be deduced that steric hindrance, which is an important factor in promoting dissociation of most *ortho*-substituted ethanes, does not play a prominent role in this case. Also in contrast to other groups a *meta* methoxyl seems to have slightly less effect than a methoxyl group in the *para* position. Symmetry of the ethane aids the dissociation, as is evidenced in the case of hexa-*o*-methoxyphenylethane. Since hexa-*m*-methoxyphenylethane is one of the first symmetrical *meta*-substituted ethanes to be studied, it is not possible to evaluate the effect of symmetry in this case.

The data also indicates that the electronegativity of the methoxyl group does not seriously aid in the degree of dissociation of the ethanes mentioned. This deduction is in line with the results obtained with halogen-substituted hexaphenylethanes.[3,4,5]

A comparison of the magnetic susceptibility and cryoscopic methods for the determination of the degree of dissociation of the methoxy-substituted ethanes was made, and the latter method was found to be inapplicable to these compounds due to the ease with which they decompose.

Bibliography

1. Gomberg, J. Am. Chem. Soc., **22**, 757 (1900).
2. Johnston, H. W., Private Communication.
3. Dietz, Thesis, Doctor of Philosophy, University of Illinois, 1941.
4. Meier, Thesis, Doctor of Philosophy, University of Illinois, 1942.
5. Himel, Thesis, Doctor of Philosophy, University of Illinois, 1942.

VITA

The writer was born in Rochelle, Illinois, on April 24, 1917. He attended grammar and high school in that city and entered Beloit College, Beloit, Wisconsin in the fall of 1935. He was granted the B.S. degree from that institution in the spring of 1939 and entered the Graduate School of the University of Illinois in September of the same year. He has continued in attendance at the University of Illinois, receiving the M.S. degree therefrom in 1941 and holding an appointment as Assistant in Chemistry for the years 1940-1942.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0208